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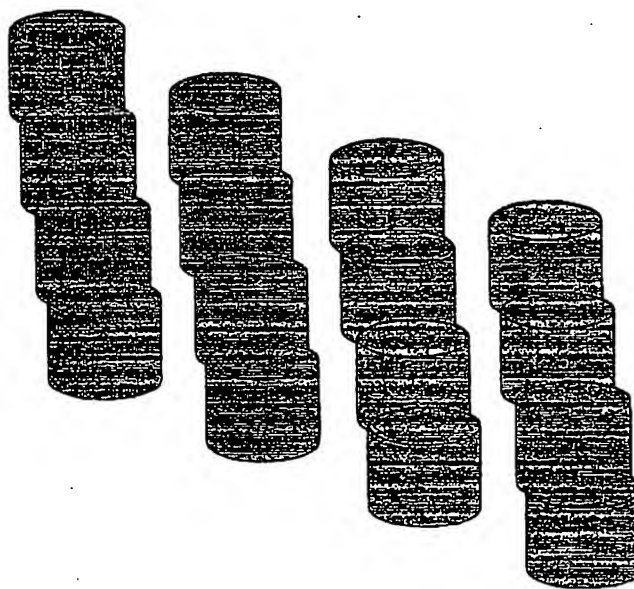
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- (71) Applicant (for all designated States except US): FORSKNINGSCENTER RISØ [DK/DK]; Frederiksborgvej 399, DK-4000 Roskilde (DK).
- (71) Applicant (for US only): BAGGER, Randi (heirress of the deceased inventor) [DK/DK]; Toftager 7, St. Valby, DK-4000 Roskilde (DK).
- (72) Inventor: BAGGER, Carsten (deceased).
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(54) Title: SOLID OXIDE FUEL CELL AS WELL AS A METHOD OF MANUFACTURING SAID SOLID OXIDE FUEL CELL



(57) Abstract: A solid oxide fuel cell for oxidation of hydrogen, coal gas or methane, and comprising a solid oxide electrolyte which is preferably formed by YSZ, and where a thin layer of anode material is attached to the electrolyte, and where a fluid flow-controlling coupling layer furthermore is placed on both the anode and the cathode side. The fluid flow-controlling coupling layer is according to the invention formed by a number of mutually separated columns 13. Such an embodiment of the coupling layer ensures a material saving. Furthermore, the height of each cell can be reduced and thereby increase the power density.



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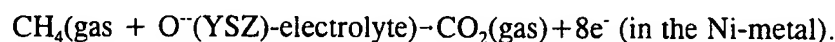
Title: Solid oxide fuel cell as well as a method of manufacturing said solid oxide fuel cell

Technical Field

The invention relates to a solid oxide fuel cell for oxidizing gases, such as methane, coal gas or hydrogen, and comprising a solid oxide electrolyte, which is preferably formed by YSZ, and where a thin layer of anode material is attached to the electrolyte, and where a fluid flow-controlling coupling layer is arranged on both the anode and the cathode side.

Background Art

10 A solid oxide fuel cell is known which comprises a solid oxide electrolyte, a solid oxide cathode and a cermet anode. The operating temperature of a stack of solid oxide cells is approximately 1000°C. The electrolyte comprises a Y_2O_3 - ZrO_2 mixed oxide, a so-called yttrium oxide-stabilized zirconium oxide (YSZ). The cathode comprises $LaMnO_3$ doped with Sr, Mg or Ca. The anode comprises a mixture of fine
15 Ni-particles and YSZ. The nickel-YSZ-oxide cermet anode is for instance produced by mixing NiO with YSZ ($Zr_{1-x}Y_xO_{2-x/2}$). This oxide mixture is sintered on the electrolyte. When the cell is activated and fuel gas is fed in form of H_2 or CH_4 to the cermet anode, NiO is reduced to Ni. Such a cermet anode must be porous in such a manner that the fuel gas can penetrate and react with the O^{2-} -ions from the YSZ
20 electrolyte while simultaneously releasing electrons to the nickel metal. Thus the anode reaction can only take place in a transition area between the three phases YSZ, Ni and fuel gas. The anode reaction is as follows:



In order to allow the electrons to be diverted, a passage or a percolation path must

exist through the Ni-phase, and for this purpose the % by volume of Ni must exceed 35%.

The use of CeO_2 based anodes implies that a reduction by means of H_2 or CH_4 results in substoichiometric CeO_{2-x} , which can conduct both electrons and oxygen ions. Such
5 an anode allows the oxidation of H_2 or CH_4 to be carried out across the entire surface, viz. the gas bordering surface, e^- and O^{2-} simultaneously being accessible across the entire surface. The latter is of importance in connection with oxidation of CH_4 , which is the main component in natural gas.

A coupling layer in form of end plates with channels for the supply of gas flows is
10 arranged on both the anode and the cathode side. These end plates involve a relatively cost-intensive manufacture because they must be made of a relatively expensive ceramic material, and furthermore they require relatively much material. In addition, they take up relatively much room and increase the height of a stack of cells to an unnecessary extent.

15 Brief Description of the Invention.

The object of the invention is to provide a solid oxide fuel cell which is less expensive to produce than hitherto known, and which in addition presents a higher power density than hitherto known.

A solid oxide fuel cell of the above type is according to the invention characterised
20 in that the fluid-controlling coupling layer is formed by a number of preferably mutually separated columns. Such a shaping of the coupling layer ensures a material saving. Furthermore, the height of each cell can be reduced and thereby increase the power density.

According to a particularly advantageous embodiment, the columns are equidistantly

arranged. The centre distance between the columns may for instance be 0.8 mm.

The invention relates also to a method of manufacturing a solid oxide fuel cell for oxidizing gases, such as methane, coal gas or hydrogen, and comprising a solid oxide electrolyte, which is preferably formed by YSZ, and where a fluid-controlling coupling layer in form of a number of mutually separated columns of ceramic material is furthermore arranged on both the anode and the cathode side. The method is characterised in that columns are stamped out of a plate of the ceramic material, where said columns may be fixed to a layer of paper, whereafter said columns are sintered after being arranged on both the anode and the cathode side. As a result a particularly simple method is obtained for the manufacture of a solid oxide fuel cell. This method provides furthermore several degrees of freedom with respect to choice of material, which is an essential factor in connection with the mechanical stresses that the materials are subjected to at the operating temperatures in question.

Brief Description of the Drawings

The invention is explained in greater detail below with reference to the accompanying drawings, in which

Fig. 1 illustrates a conventional fuel cell arranged between two coupling layers with gas channels,

Fig. 2 illustrates a coupling layer in form of a high number of columns of ceramic material,

Fig. 3 illustrates how the ceramic material can be manufactured,

Fig. 4 illustrates how the ceramic material can be formed into columns,

Fig. 5 shows the stamping tools used for this purpose,

Fig. 6 illustrates a single column,

Figs. 7 and 8 show photomicroographies of stamped column layers.

Best Mode for Carrying Out the Invention

5

Fig. 1 illustrates a known solid oxide fuel cell comprising an anode in form of a layer of Ni-YSZ-cermet, a layer of a YSZ-electrolyte 2 and a cathode 3 in form of a layer of La(Sr)MnO₃. The thickness of both the electrodes and the electrolyte is typically 100 μ m. Considerable variation possibilities do, however, apply, from a few μ m and up to 0.3 mm for the electrolyte and up to 1 mm for the electrodes. An Ni-YSZ-anode is not particularly suited for oxidation of CH₄, and it has therefore been replaced by a CeO₂-based anode 4.

One measure of preventing CeO₂ from diffusing into YSZ is to add NiO or another transition metallic oxide or auxiliary oxide surfactive on YSZ to CeO₂. Another measure is to paint a layer of such a metallic oxide powder suspended in a dispersant on the YSZ electrolyte 2, whereafter the CeO₂ powder is applied. The expression surfactive is to be construed such that the auxiliary oxide, such as MnO₂ or NiO, is easy to distribute uniformly across the YSZ surface, and that the following heat treatment does not cause said auxiliary oxide to get lumpy on the surface. The measure can optionally be carried out by mixing up to 30% by weight of NiO into the CeO₂-based ceramic powder. It is assumed that a much lower content of NiO suffices. Other possible auxiliary oxides are oxides of the transition metals V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Nb, Ta and of Ga, Ge, In, Sn, Sb, Pb and Bi.

The effect of the auxiliary oxide is that the YSZ surface is completely covered by said auxiliary oxide and thereby prevents CeO₂ from diffusing into YSZ, and further-

more that said auxiliary oxide almost glues YSZ and CeO_2 together in connection with a low interfacial tension between said YSZ and CeO_2 . In order to be usable in a solid oxide fuel cell, the auxiliary oxide layer serving as glue layer must be penetrable to oxygen ions when the fuel cell operates. The use of NiO as auxiliary oxide has the effect that during the starting procedure NiO is likely to be reduced to metallic Ni at the interaction of hydrogen. As the molar volume of Ni is no more than $6.6 \text{ cm}^3/\text{mole}$, and as the molar volume of NiO is $11.2 \text{ cm}^3/\text{mole}$, a considerable contraction takes place. As a result CeO_2 is brought into direct contact with YSZ, whereby O^- ions fairly freely can move from YSZ into CeO_2 .

10

If the Ni resulting from the reduction of NiO appears on the CeO_2 surface as particles of a diameter of approximately $1 \mu\text{m}$ or more, problems are likely to arise in connection with the oxidation of CH_4 , Ni being a well-known cracking catalyst. Ni exposed to CH_4 at 1000°C is therefore assumed to cause a liberation of coal, which gradually destroys the anode. In order to avoid the latter, it is possible to ensure that no Ni on the whole is visible on the CeO_2 surface, for instance by NiO only being applied as a layer on the YSZ electrolyte and not mixed with CeO_2 . Such a procedure can for instance also be obtained by allowing the Ni-metal to be exposed to CH_4 at the surface and by treating said surface with H_2S in return at the start. When Ni is exposed to H_2S at 1000°C , an NiS layer is formed on the Ni particles with the effect that the cracking-catalytic properties no longer apply. As a result it is possible to improve the conductivity of the CeO_{2-x} electrode by adding up to 35 to 40% by weight of Ni. The treatment with H_2S has the effect that the ability of Ni to liberate coal from CH_4 in connection with cracking is eliminated.

25 Compared to an Ni-YSZ cermet electrode, an Ni- CeO_{2-x} electrode treated with H_2S tolerates a possible sulphur content in CH_4 . An essential problem associated with the classic Ni-YSZ cermet is that it is inactivated if it is exposed to a sulphur content in the fuel gas of the magnitude 100 ppm for a prolonged period of time. Ni-free CeO_2 -based electrodes are also assumed to tolerate sulphur.

A particular problem associated with CeO_2 based electrodes 4 is that such CeO_{2-x} electrodes are often damaged because some of the O^{2-} -ions are removed from the CeO_{2-x} crystal lattice while some of the Ce^{+4} -ions are reduced to Ce^{+3} . As a result the crystal lattice expands both because less negative O^{2-} -ions are present to keep the positive Ce-ions together and because a Ce^{+3} -ion is larger than a Ce^{+4} -ion. Apparently, a solution of the latter can be found as well.

When CeO_2 is doped with a tri or divalent metallic oxide, such as Y_2O_3 or CaO , solid solutions are formed, said solutions being of the type



or $\text{Ce}_{1-x}\text{Ca}_x\text{O}_{2-x}$. Once a deficiency of oxygen ions, viz. oxygen ion vacancies, is introduced into the $\text{Ce}_x\text{Ca}_x\text{O}_{x-2}$ crystal lattice, it is rather difficult to achieve further oxygen ion vacancies as a result of the reduction of Ce^{+4} to Ce^{+3} . The process is as follows:



where the vacancies form part as species to the same extent as the ions in the crystal lattice. In other words, already introduced vacancies from a CaO doping displace the equilibrium towards the left.

When the formation of Ce^{+3} and vacancies is slowed down by the addition of CaO , the electronic conductivity of the CeO_2 -based electrode is reduced because the electronic conductivity derives from the outermost, loosely arranged electron in the Ce^{+3} -ion. Accordingly, when the Ce^{+3} concentration is reduced, the conductivity is reduced as well. In order to increase the conductivity of the electrons it is possible

to add substances, such as Nb_2O_5 , where Nb^{+5} is reduced more easily than Ce^{+4} . Also in Nb^{+4} the outermost, loosely arranged electron is mobile. A measure of increasing the volume stability of CeO_2 is to dope with metallic oxides, where the metallic ion is smaller than Ce^{+4} . As a result, local stresses, viz. deformations, are introduced in CeO_2 capable of absorbing local increases in the volume, said increases arising during the formation of Ce^{+4} through a reaction with Ce^{+3} .

The substances dopable to CeO_2 in order to improve the conductivity of the electrons are for instance Nb_2O_5 , Ta_2O_5 , TiO_2 , P_2O_5 , As_2O_5 , Sb_2O_5 , $\text{Bi}_2\text{O}_3\text{SnO}$, In_2O_3 and SO_3 or mixtures thereof or substances resulting in the same mixture by an addition of CeO_2 followed by a heat treatment, such as the carbonates of the same metals or for instance $\text{Ce}(\text{SO}_4)_2$ in stead of SO_3 or CePO_3 in stead of P_2O_5 .

The substances dopable to CeO_2 in order to improve the stability of the volume by way of reduction are metallic oxides, where the metallic ion is mono, di or trivalent, such as Na_2O , K_2O , MgO , CaO , SrO , BaO , Sc_2O_3 , Y_2O_3 , La_2O_3 , In_2O_3 , Ga_2O_3 as well as tri and divalent lanthanides, Ti_2O_3 , ZnO , Al_2O_3 . Oxides with metallic ions smaller than Ce^{+4} are apparently particularly suited.

Fig. 1 illustrates the individual fuel cell repeated in a stack. The fuel cell comprises a first end plate 9 with some channels 10 for a gas flow, a fuel electrode 4, an electrolyte, an air electrode and a second end plate 11 with channels 12 extending transverse to the channels in the first end plate. The fuel gas is fed to the cells at a pressure of approximately 1 to 10 atm. It can for instance be a cell stack in a manifold, cf. Fig. 4 showing the inlet and outlet openings 5, 6, 7, 8 for air and fuel gas, respectively. Furthermore, some flow-controlling coupling layers of a wavy material 13 are shown, said coupling layers providing some elongated channels for fuel gas and air, respectively. As a result, the flow direction of the air extends transverse to the flow direction of the fuel gas. The voltage across each cell is approximately 0.7 V at an operating temperature of approximately 1000°C. Below it has been shown

how the operating temperature can be lowered, cf. Danish Patent Application No. PA 1999 00623.

The flow-controlling coupling layers are according to the invention formed by column layers, cf. Fig. 2. Each column layer comprises a number of columns 13, which
5 are preferably mutually separated. The columns 13 may be of almost any arbitrary dimension and be arranged according to desire. However, the columns 13 are preferably cylindrical, and they are preferably equidistantly arranged with a centre distance of approximately 1.8 mm.

A manufacturing method has been developed, whereby columns of a height of 0.5
10 to 1.0 mm and a diameter of 1 mm are embossed in of ash-less paper. The manufacturing method is illustrated in Fig. 3 and has been optimized in such a manner that the waste of material has been reduced to almost zero. The column layer of the ash-less paper can be handled, and the paper burns during sintering with the result that the columns 13 are left in the desired arrangement provided said procedure is carried
15 out at a suitable load.

A water-based binder system is used, said binder system comprising methyl-hydroxy-ethyl-cellulose (Tylose MH300P, Hoechst or Tylose MH 300P2, Clariant) and polyethylene glycol 400 (PEG for synthesis, Merck-Schuchardt). The procedures used for mixing the viscous masses are shown in Fig. 3. The dry mixture
20 is subjected to a ball milling in a bottle of polypropylene. The desired amounts of water are added during mixing in either a Z-mixer (Werner und Pfleiderer Type LDUK 3IInS) for one hour or by hand mixing. Examples of used plastic compositions are indicated in Table 1. The grain size of the precursor powder is, however, not critical.

Table 1

Examples of composition of used viscous masses.

MASS	ACC	CCC	COMPOSITION											
			NiO		8YSZ		Coarse		LSM [§]	PEG	Tylose	H2O		
			Raw	Calc.	Fine	Coarse	wt %	wt %					wt %	wt %
5	NYZ-99-1	*	-	41.3	6.5	26.2*	-	4.4	5.0	16.6				
	NYZ-99-2	*	41.9	-	6.6	26.4*	-	4.6	5.0	15.5				
	LSM-99-2	*	-	-	-	-	72.4	5.5	3.3	18.7				
	LSM-99-3	*	-	-	-	-	59.5	4.5	2.7	38.1				

9

*: Tosoh TZ-8Y, calcined at 1400°C, $d_{50\%} = 28 \mu\text{m}$ & $d_{\text{max}} = 45 \mu\text{m}$ 10 §: $\text{La}_{0.71}\text{Sr}_{0.3}\text{Mn}_{1.05}\text{O}_3$, $d_{50\%} = 5 \mu\text{m}$

The plastic masses were shaped into sheets of a thickness of approximately 1 mm using a roller machine (Cavallin model 013) equipped with an Omron Sysdrive 3G3HV inverter for adjusting the roller speed. During the rolling, the masses were wrapped in plastic film (Vita Vrap) in order to minimize the evaporation of water.

- 5 The sealed masses were furthermore rolled in a polyethylene bag (HDPE 70 μm) in order to avoid the curlings which might otherwise arise during the rolling of the thin sheets. During the rolling, the sheets were cut into desired dimensions and dried by one of the following procedures.

1. The cut sheets were placed between glass plates and dried at 60°C 75% RH for
10 more than 24 hours. The final drying was carried out at 120°C until the weight was constant, corresponding to 0.5% by weight of H_2O .

2. Initially the cut sheets were dried in a microwave oven (Ide Line MI-2072, output power of approximately 34 W and a frequency of 2,450 MHz), where at least 4.5% by weight of water were removed. Some supports were then placed between
15 the glass plates and dried at 110°C for 17 to 24 hours (corresponding to a H_2O residue of approximately 0.5% by weight).

By the above drying procedures, the flatness of the resulting plate depended on the flatness of the plates between which the viscously processed plates were dried. The used glass plates have a flatness of $\pm 25 \mu\text{m}$). These processed plates are used di-
20 rectly for stamping columns out of the green ceramic layer in a 200 μm thick ash-less paper 15, such as Whatman Cat. No. 141 150. This stamping renders it possible to fix the columns 13 in the ash-less paper 15. In this manner the column layers can be manufactured in desired arrangements. The ash-less paper 15 is removed during the following heating, such as in a cell stack.

- 25 Some moulds for stamping out the columns 13 are shown in Fig 4. One mould A comprises a perforated steel plate, cf. Fig. 4, for providing a layer of a number of

columns arranged in a matrix. Sprigs 17 in the lower mould have a diameter of 1.1 mm and are placed with a minimum distance of 0.3 mm. Some springs of a diameter of approximately 1 mm are optionally provided in some corresponding holes in superposed mould B.

5 The entire stamping arrangement comprises the following parts, cf. Figs. 4 and 5:

- A flat bottom 18 with four holes for the fixation of some steel columns 14 of a diameter of for instance 1 cm.
- 4 fixation columns 14 of a diameter of for instance 1 cm.
- Superposed moulds optionally comprising springs in the desired arrangement. The
10 springs are of a diameter which is 15% smaller than the desired diameter, and they are of a height of for instance 4.3 mm.
- Three perforated intermediate steel plates A, B and C, where the holes are 0%, 10% and 30%, respectively, larger than the desired column diameter.
- Metal rings for the fixation columns 14 for adjusting the distance between the
15 springs, if any, and the perforated plate C so as to provide sufficient room for the columns stamped out.

The perforated plate A is used for removing excess, viscously processed plate from the mould after the stamping out, cf. Fig. 5d. The use of such a plate implies that it is not necessary to require additional cleaning of the mould, and the excess material
20 can be recycled merely by addition of water. The perforated plate B is used for stamping out the columns 13. The diameter of the holes of this plate B determines the diameter of the columns 13 being stamped out. The perforated steel plate C is used for supporting the ash-less paper 15 during the stamping procedure.

The first step of the manufacturing process is to adjust the ash-less paper 15. A viscously processed plate 20 is then positioned between the two plates A and B. The paper 15 in question and the perforated steel plate C are then placed atop the plate B. The fixation columns 14 serve to fix the plates relative to one another. The superposed mould with the springs is subsequently mounted. Now the stamping out procedure can be carried out either by means of a rubber hammer or by pressing the stamping parts against one another by means of a uniaxial press.

During the stamping procedure the sprigs 17 are pressed upwards into the ceramic plate. As a result, the ceramic columns are provided which are retained in the holes provided in advance in the paper layer. These ceramic columns simply stick to said paper layer.

The water content of the viscously processed plate is important for the final result. Cylindrical columns 13 are provided by means of dry or almost dry plates, said columns 13 having a thickened foot if the plate contains too much water.

Not totally dry plates result in plates which are sensitive to the pressure by which the stamping is performed. Photomicrographies of columns layers stamped out appear from Figs. 7 and 8. The columns illustrated in Fig. 8 are made of a dry, viscously processed plate which has been dried at 110°C. At the bottom side these columns 13 disclose some cracks, cf. Fig. 8B, caused by a dry precursor plate. However, the cylindrical shape of the columns 13 is easier to obtain by means of dry plates than by means of not totally dry plates. However, the ash-less paper 15 curls during the heating. Therefore, the individual columns 13 cannot maintain their position unless the sintering procedure is performed at a predetermined load, such as by a sintering of the LSM CCC-layer in a stack during the first heating period. A sintering of the column layer which is green by a load of 4.5 to 24.5 kPa at 850 to 1000°C for two hours results in a column layer with a desired arrangement of the columns 13.

When a complete cell stack is to be provided, a layer of paper with columns is placed atop each cell. Then a disk of metallic interconnect is placed thereon followed by a sheet of paper with columns. These four elements are repeated. A stack of such elements is assembled, where one element is metallic, the second element is a sintered cell and the two remaining elements are soft non-sintered column elements. Now follows a heating to the operating temperature. Not until now organic components, such as a binder, disappear. During the heating to the operating temperature, the organic components adjust to their abutting surfaces, and the materials start to sinter together. The binder and the softener disappear as well during the heating to the operating temperature of 600°C.

Flow-controlling means can, if desired, be provided between the columns 13, said flow-controlling means comprising strings of a cylindrical or polygonal cross section and optionally being manufactured by way of extrusion of the binder-bound column material or by way of casting of strings with glass-bound sealing materials and arranged in the column plane. The strings can be mounted in the flow spaces between the columns a) in the existing spaces in the uniform column pattern, b) after removal of the columns where the strings are to be mounted, or c) after omission of the column extrusion where the flow-controlling strings are to be mounted.

The flow-controlling means render it possible to establish flow patterns optimizing the general design with respect to minimizing undesired effects, such as a) local temperature gradients caused by uneven area-specific effect development or power consumption, or b) admixing of fluids or gases from the two electrode sides where said fluids or gases may come into contact with one another.

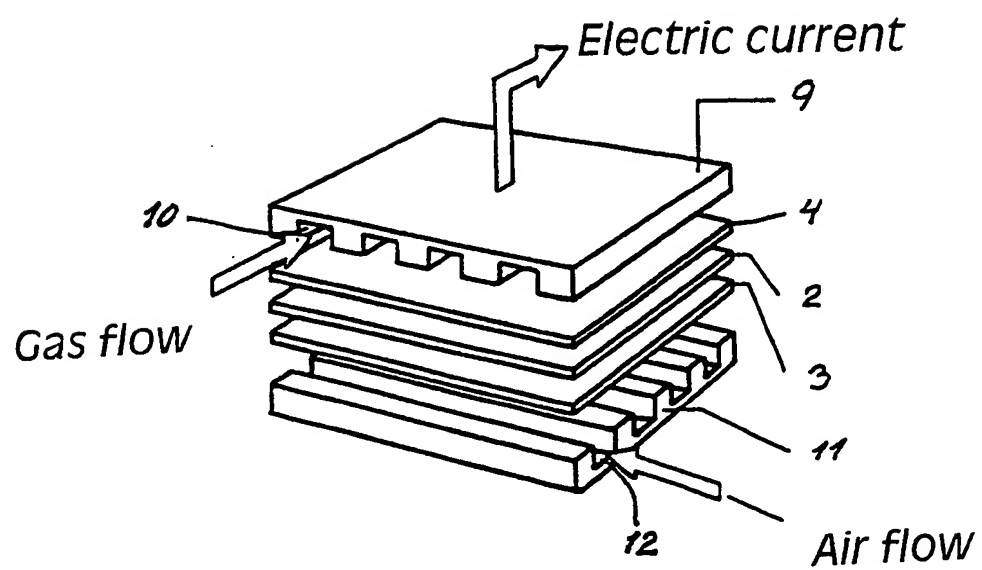
Some of the sprigs can optionally be removed in response to the fluid-controlling means to be inserted.

Claims

1. A solid oxide fuel cell for oxidation of gases, such as methane, coal gas or hydrogen, and comprising a solid oxide electrolyte, which is preferably formed by YSZ, and where a thin layer of anode material is attached to the electrolyte, and
5 where a fluid flow-controlling coupling layer is arranged on both the anode and the cathode side, c h a r a c t e r i s e d in that the fluid flow-controlling coupling layer is formed by a number of preferably mutually separated columns (13).
2. A solid oxide fuel cell as claimed in claim 1, c h a r a c t e r i s e d in that the columns (13) are equidistantly arranged.
- 10 3. A solid oxide fuel cell as claimed in claim 2, c h a r a c t e r i s e d in that the centre distance between the columns (13) is approximately 1.8 mm.
4. A solid oxide fuel cell as claimed in one or more of the preceding claims, c h a r a c t e r i s e d in that each column (13) is of a height of approximately 0.5 to 1.0 mm.
- 15 5. A solid oxide fuel cell as claimed in one or more of the preceding claims, c h a r a c t e r i s e d in that each column (13) is of a diameter of approximately 1.0 mm.
6. A solid oxide fuel cell as claimed in one or more of the preceding claims, c h a r a c t e r i s e d in that flow-controlling means are provided between the
20 columns (13).
7. A solid oxide fuel cell as claimed in one or more of the preceding claims, c h a r a c t e r i s e d in that the columns (13) are made of a ceramic material or a mixture of ceramics and metal.

8. A method of manufacturing a solid oxide fuel cell for oxidation of gases, such as methane, coal gas or hydrogen, and comprising a solid oxide electrolyte, which is preferably formed by YSZ, and where a fluid-controlling coupling layer in form of a number of mutually separated columns of a ceramic material furthermore is
5 placed on both the anode and the cathode side, c h a r a c t e r i s e d in that a stamping out of columns from a plate of the ceramic material is performed, where said columns may be fixed to a layer of paper, whereafter the columns are subjected to a sintering after being placed on both the anode and the cathode side.
9. A method as claimed in claim 8, c h a r a c t e r i s e d in that the columns are
10 subjected to a mechanical load during the sintering.
10. A method as claimed in claim 9, c h a r a c t e r i s e d in that the columns are subjected to a mechanical load of 4.5 to 24.5 kPa at a temperature of 850 to 1000°C for approximately two hours during the sintering.
11. A method as claimed in claims 8 to 10, c h a r a c t e r i s e d in that an
15 interconnect disk is placed on the columns.

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*Fig. 1*

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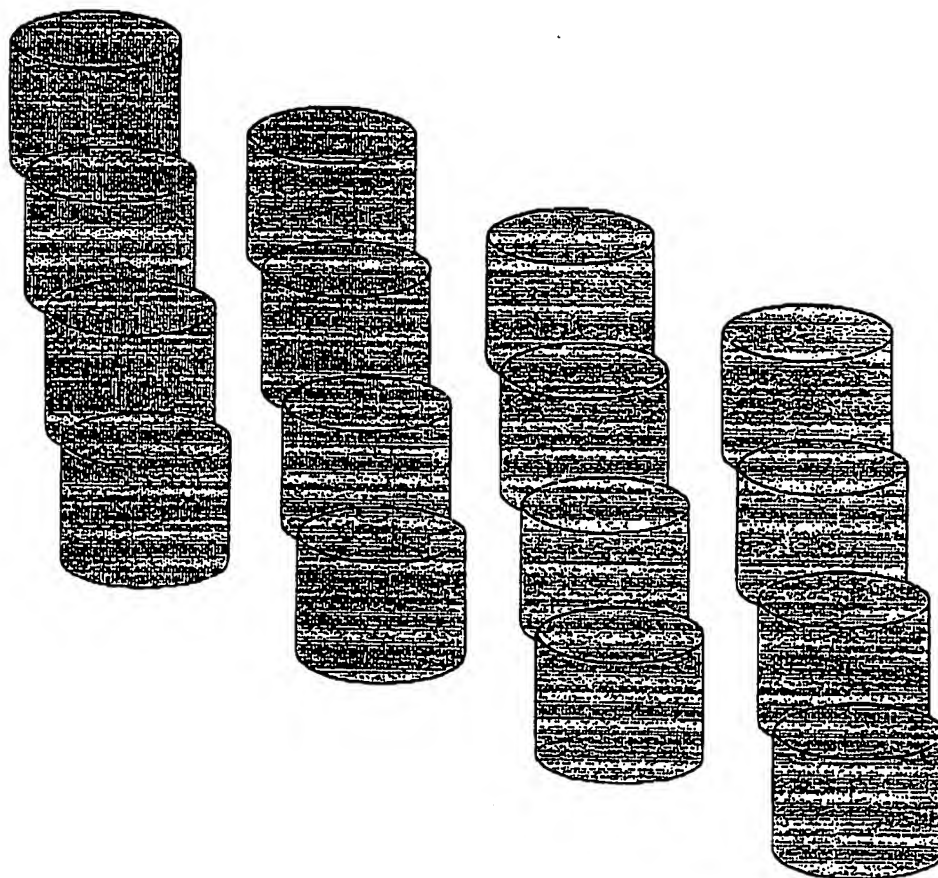
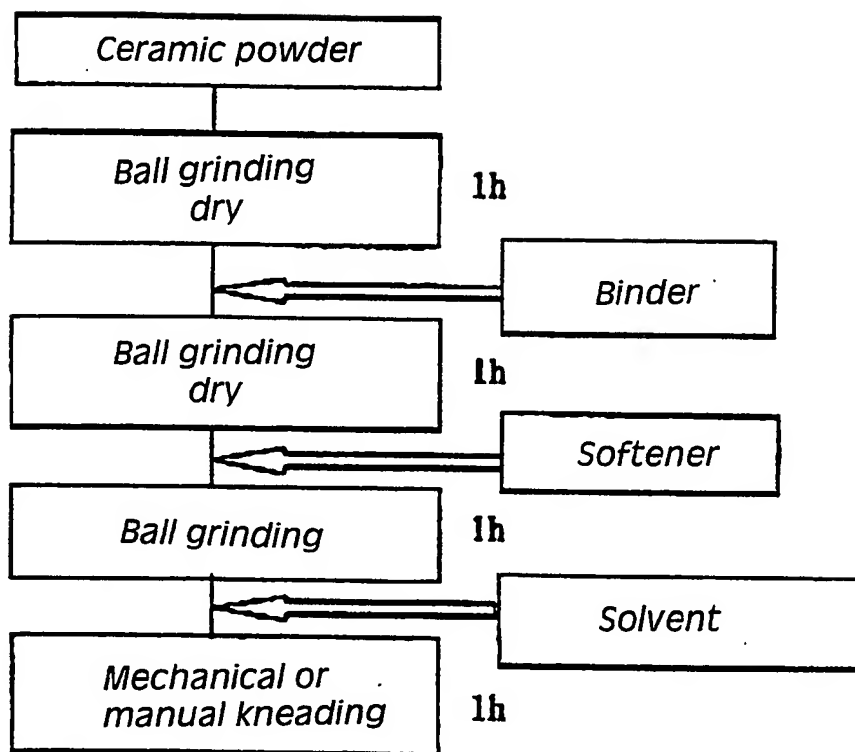
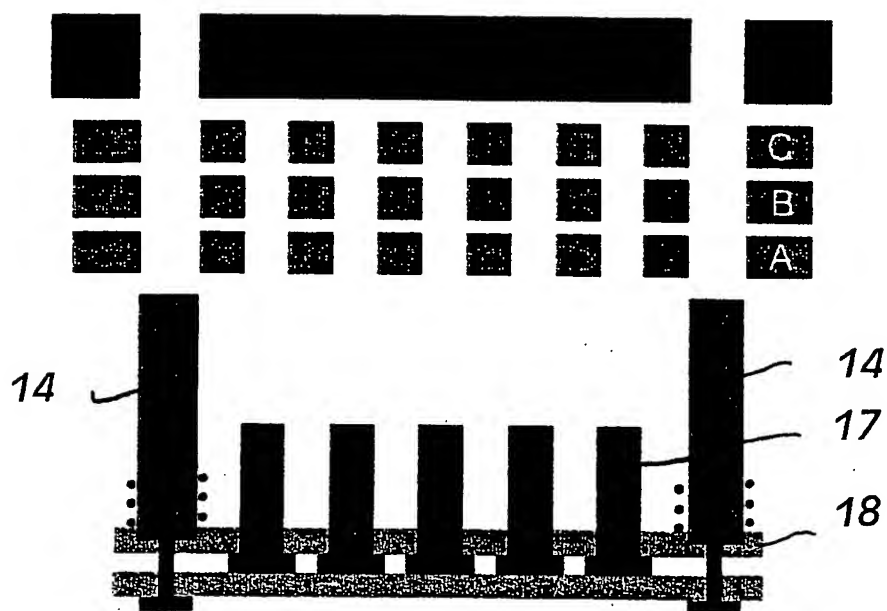
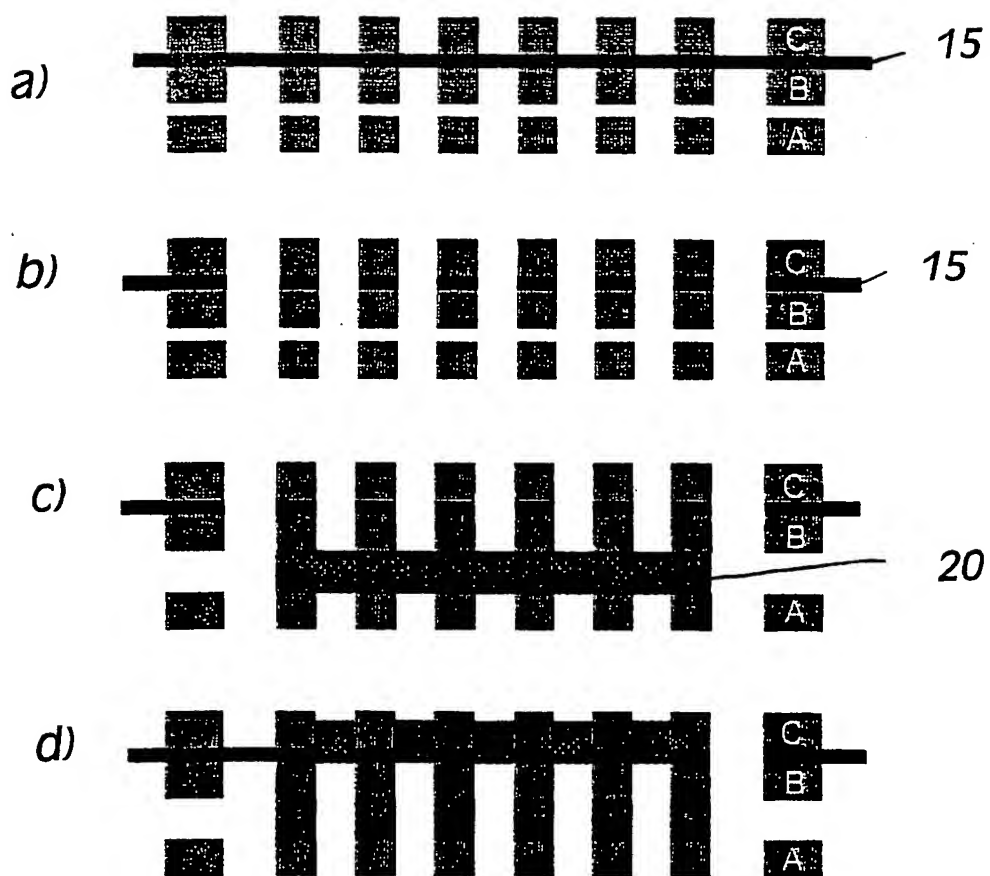


Fig. 2

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*Fig. 3*

*Fig. 4*

*Fig. 5*

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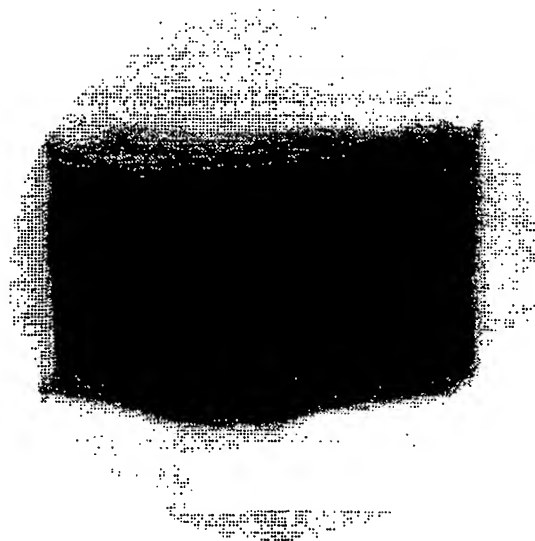


Fig. 6

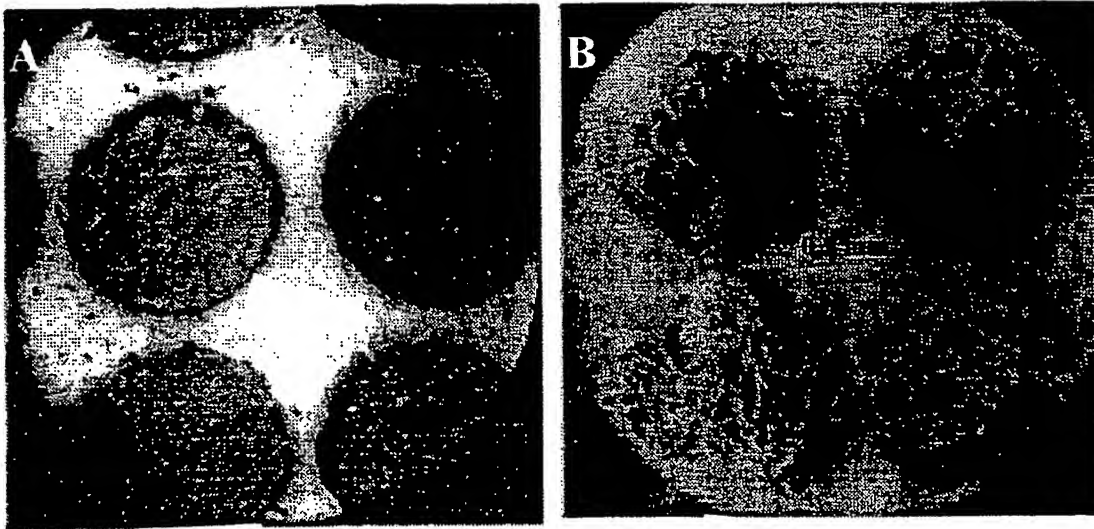


Fig. 7

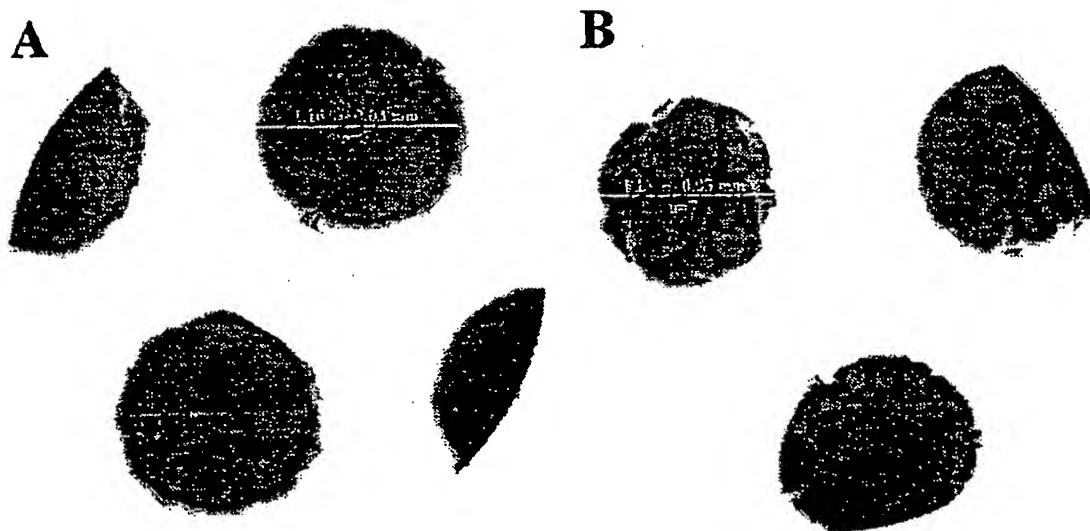


Fig. 8

INTERNATIONAL SEARCH REPORT

International application No.

PCT/DK 01/00157

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: H01M 8/12, H01M 8/24

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-INTERNAL, WPI DATA, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 9209116 A1 (ALLIED-SIGNAL INC.), 29 May 1992 (29.05.92), page 6, line 20 - page 7, line 4 --	1
A	EP 0974564 A1 (SULZER HEXIS AG), 26 January 2000 (26.01.00), column 3, line 29 - line 40 -----	1-11

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

8 June 2001

Date of mailing of the international search report

03.07.01

Name and mailing address of the ISA:

European Patent Office

Authorized officer

Ulla Granlund/MP

Facsimile No.

Telephone No.

SA 52167

INTERNATIONAL SEARCH REPORT
Information on patent family members

30/04/01

International application No.
PCT/DK 01/00157

Patent document cited in search report			Publication date	Patent family member(s)		Publication date
WO	9209116	A1	29/05/92	US	5256499 A	26/10/93

EP	0974564	A1	26/01/00	AU	4109299 A	24/02/00
				JP	2000053424 A	22/02/00
